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PHOTOADSORPTION AND PHOTODESORPTION OF OXYGEN ON INORGANIC SEMICONDUCTORS AS INVESTIGATED BY ESR

By

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Abstract

Changes were investigated in ESR spectra of adsorbed oxygen species and of paramagnetic species on/in the semiconductor such as ZnO, TiO₂ and ZrO₂, when the solids were irradiated, and combined with simultaneous measurements of the quantity of oxygen adsorbed or desorbed. Experimental evidences are presented for the photoadsorption and photodesorption of oxygen, as affected by the pretreatment of the semiconductor sample, ambient oxygen pressure and wavelength of the light.

The result suggests that photoadsorption and photodesorption of oxygen are general phenomena at least for the semiconductors investigated and that the direction of photoresponse is controllable by the position of the Fermi level of the sample and by the quantity of neutral oxygen molecule present on the surface. It is suggested also that both electrons and positive holes participate in the phenomena.

Introduction

Photoadsorptive, photocatalytic and photoconductive properties of inorganic semiconductors have been recognized for a number of years. Photoproduced electrons and holes in the semiconductors presumably interact with adsorbed species, modifying the rate of surface reaction while they may give rise to photocurrent. For example, it is well known that suspensions of ZnO in water produce hydrogen peroxide when irradiated with ultra violet lights.¹⁾ Also, the anodic oxidation of *n*-type germanium under photoirradiation is known to proceed much faster than for *p*-type.²⁾ The latter phenomenon is particularly interesting, because according to BRATTAIN and GARRETT²⁾ positive

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holes are considered to play an important role in the photooxidation of *n*-type germanium. Experimental evidence indicative of the role of adsorbed oxygen on the photocurrents in semiconductors has been given by MYASNIKOV and PSHEZHETSKII,³⁾ MELNICK⁴⁾ and MEDVED⁵⁾ with respect to ZnO; it was considered by these workers that *negative* or *positive* photocurrent is closely related with photoadsorption or photodesorption of oxygen. However, most of the results were quite qualitative in character.

During the recent years, a variety of inorganic semiconductors have been shown to give photoexcited-adsorption or -desorption of adsorbed gases. Several examples are illustrated in Table 1.

TABLE 1. Photoeffect on various adsorbent-adsorbate systems.

+ : photoadsorption, - : photodesorption

| | | | |
|--------------------------------------|------|---|------|
| ZnO-O ₂ ^{6,7,8)} | +, - | ZnO-H ₂ ¹⁴⁾ | + |
| ZnO(Al)-O ₂ ⁹⁾ | - | TiO ₂ -O ₂ ¹⁰⁾ | + |
| ZnO(Li)-O ₂ ⁹⁾ | + | CdS-O ₂ ⁹⁾ | + |
| ZnS-O ₂ ¹³⁾ | + | CdSe-O ₂ ¹¹⁾ | +, - |
| ZnO-CO ⁷⁾ | + | NiO-O ₂ ¹²⁾ | - |

As shown in Table 1, photoadsorption of oxygen takes place on one semiconductor while it gives way to photodesorption on another semiconductor; why does this happen? In this connection, it is interesting to note that photoadsorption of oxygen on ZnO is reported to occur only when the sample is in an *oxidized* state while photodesorption occurs on a *reduced* sample.⁶⁾ We considered that the direction of the photoresponse is determined by the Fermi level of the ZnO sample. Experiments were carried out by us on doped ZnO samples, and it was found that ZnO(Al) gives rise to photodesorption of oxygen whereas ZnO(Li) photoadsorption (Table 1). Such dual character of photoresponse on ZnO was confirmed later by TEREIN and SOLONITZIN⁷⁾ as well as by BARRY and STONE.⁸⁾

In the meantime, the work of Professor WOLKENSTEIN^{15,16,17,18)} came to our notice. The problem of photoadsorption and photodesorption was analyzed by him on the basis of the general concepts of the electron theory of semiconductors. Two types of adsorbed state; *weak* and *strong* or *neutral* and *charged* were assumed, and the dual character of the photoeffect was shown to be affected by the position of the Fermi level of the semiconductors. The theory thus appeared to be in harmony with the experiments.

Photoadsorption and photodesorption of gas have been determined so far by measuring the change of residual gas pressure due to photoirradiation.

Photoadsorption and Photodesorption of Oxygen

We have little knowledge about the kind and behavior of adsorbed gases. It seemed worthwhile, therefore, to investigate the photodynamical behavior of adsorbed gases on semiconductors, and it is needless to say that electron spin resonance (ESR) technique should provide important information.

In the present paper, the authors will report some general aspects of photoadsorption and photodesorption of oxygen on ZnO, TiO₂ and ZrO₂ as investigated by ESR.

Experimental

The ESR measurement was carried out by JEOL-P-10 (X-band 100 kC modularion) spectrometer with semiconductor samples kept usually at room temperature. Absolute spin density calibrations were made by Mn²⁺ in MgO directly inserted in the sample tube and by DPPH in benzene. A quartz tube of 4 mm internal diameter, containing 0.1-0.4 g of a semiconductor sample, was connected to a high vacuum line and equipped with a Pirani gauge near the tube. Special care was taken to protect the semiconductor sample from the vapour of stopcock grease with a trap of liquid nitrogen which also served as a bath for the Pirani gauge.

A change of the electric conductivity of a semiconductor sample alters the cavity Q which in turn is indicated by a change in the bias current of the crystal detector of the microwave power. For example, ZnO of high conductivity may give rise to a large loss of microwave power, and adsorbed oxygen is known to reduce the conductivity of ZnO and results in a higher Q and a negative change in the crystal current.¹⁹⁾ We shall utilize the change of the crystal current to obtain information about electron transfer between the bulk of ZnO and adsorbed oxygen species in the absence and presence of ultra violet irradiation.

A 500 W super high pressure mercury lamp was used as a light source combined with various glass filters (Toshiba Co.) or with a saturated CuSO₄ solution.

ZnO: A powdered ZnO sample, supplied by New Jersey Zinc Co. (S.P. 500) was used. TiO₂: A TiO₂ sample was prepared by hydrolysing TiCl₄, manufactured by Koso Chemical Co., with ammonia and then by drying it at 130°C. The sample was then calcined at 500°C in a stream of oxygen to provide a white sample of anatase type. ZrO₂: A powdered sample, purchased from Merck Co., was used.

All semiconductor samples were outgassed, unless otherwise stated, at 500°C in high vacuum (10⁻⁵ Torr) before the measurements.

Results and Discussion

3-1 Photoadsorption and Photodesorption of O_2 on ZnO

ESR Spectrum of ZnO- O_2

As already reported by many workers,²⁰⁻²⁹⁾ the ESR spectrum of ZnO adsorbed by oxygen (denoted as ZnO- O_2) consisted of a $g=1.96$ signal due to conduction electrons and/or electrons in a donor level, and an anisotropic signal near $g=2.0$ due to adsorbed oxygen species. The latter signal was characterized by three g -values: $g=2.002$, 2.008 and 2.049 ^{23,26,27)} and assigned to the molecular oxygen ion, O_2^- , as will be discussed later. The spin density of these signals per g ZnO will be denoted as $I_{1.96}$ and $I_{2.0}$ respectively.

To obtain information concerning electron transfer between the bulk of ZnO and adsorbed oxygen species, we have investigated¹⁹⁾ the change of $I_{1.96}$ and $I_{2.0}$ together with that of the crystal current, ΔCC , against the degree of oxygen adsorption per g ZnO at room temperature. The result is shown in Fig. 1.

The decreasing curves for $I_{1.96}$ and ΔCC are in accordance with the known fact that adsorbed oxygen accepts electrons from the bulk of ZnO.

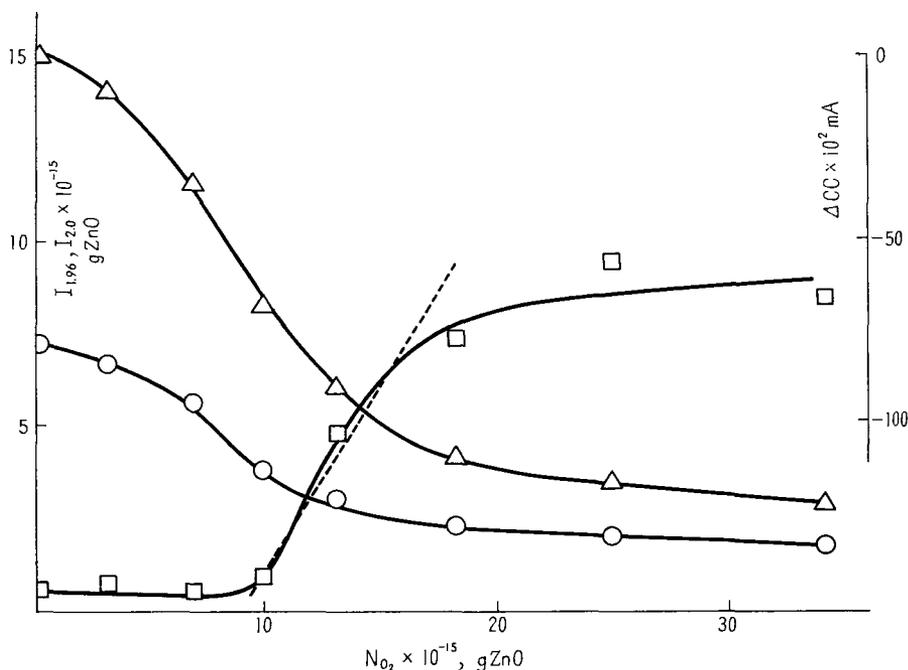


Fig. 1. Dependence of $I_{1.96}$ (○), $I_{2.0}$ (□) and ΔCC (△) on N_{O_2} .

Photoadsorption and Photodesorption of Oxygen

As shown in Fig. 1, $I_{2.0}$ appeared to increase only above the oxygen coverage of about 1×10^{16} molecule/g ZnO, suggesting that oxygen species of no observable resonance is formed on the surface at lower coverages. A similar result was reported also by SANCIER.²⁵⁾ At coverages exceeding about 2×10^{16} , the change of all the ESR parameters was less dependent on the oxygen coverage; neutral oxygen species seem to be adsorbed exclusively.

Let us consider the nature of the triplet signal near $g=2.0$ which appears only within the limited range of coverage. In this range it should be particularly noted that $I_{2.0}$ increases with an increase of the adsorbed quantity of oxygen, N_{O_2} , in a ratio of one spin per one adsorbed oxygen molecule. The dotted line of Fig. 1 shows such a slope.

Thus, except at lower and higher coverages, it seems very probable that one adsorbed oxygen molecule produces one paramagnetic species of the $g=2.0$ triplet signal. Recently, such a correspondence was also suggested by LUNSFORD.³⁰⁾ The result of a microwave power saturation experiment, in the range of 8–250 mW, indicated that the signal originated from a common species in accordance with the communication of FUJITA and TURKEVICH.³¹⁾

Since experimental data, including those of Fig. 1, indicated that $I_{1.96}$ and ΔCC are linearly correlated over the entire range of surface coverages investigated, for subsequent discussions we shall indicate the observed changes of $I_{1.96}$ and ΔCC per one adsorbed oxygen molecule or molecular ion. The values are listed in Table 2.

TABLE 2. Approximate values showing dependence of $I_{1.96}$ and ΔCC on oxygen coverage.

| | $N_{O_2} < 1 \times 10^{16}$ | $1 \times 10^{16} < N_{O_2} < 2 \times 10^{16}$ | $N_{O_2} > 2 \times 10^{16}$ |
|---------------------------|------------------------------|---|------------------------------|
| $\Delta I_{1.96}/N_{O_2}$ | ~ 0.64 | ~ 0.26 | very small |
| $\Delta CC/N_{O_2}$ | 13×10^{-17} | 7×10^{-17} | very small |

Photoadsorption under High Oxygen Pressure

Let us examine the effect of photoirradiation on the crystal current. In Fig. 2 is shown the change of the crystal current, ΔCC , of ZnO when irradiation was carried out at wavelengths ranging from 350 to 450 $m\mu$ corresponding to the forbidden gap. The abrupt increase of ΔCC is associated with production of conduction electrons. When the ZnO, originally at 10^{-5} Torr O_2 , was exposed to 20 Torr oxygen pressure during irradiation, ΔCC decreased immediately but not to the original value. Subsequent evacuation of the system in the absence of irradiation little affected the crystal current. This result

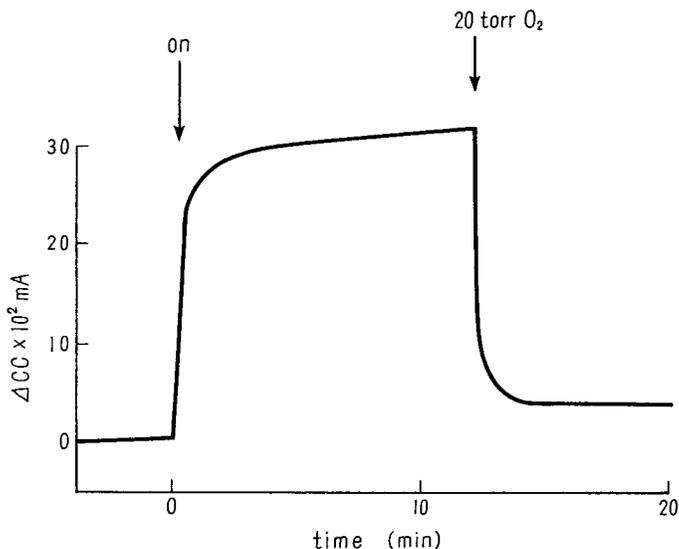
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Fig. 2. Changes of CC due to photoirradiation and subsequent exposure to 20 Torr O_2 (ZnO).

suggests that photoproduced electrons are irreversibly trapped by the added oxygen, that is, photoadsorption of oxygen occurred.

The phenomena were investigated more in detail. Photoirradiation was made on ZnO under 20 Torr oxygen, and changes of $I_{2.0}$ before and after the irradiation were observed while the crystal current was recorded. The measurement of $I_{2.0}$ was carried out after pumping off the residual gaseous oxygen at room temperature in a short period of time to avoid the pressure broadening effect. However, some neutral oxygen is believed to remain on the surface of the ZnO. The result is shown in Fig. 3 a and Table 3.

As shown in Fig. 3 a, both ΔCC and $I_{2.0}$ increased on irradiation; the $g=2.0$ triplet signal became 1.5 times as large as the one obtained in the dark. This value is expected to correspond to the decrease of both the crystal current, 31×10^{-2} mA, and the $g=1.96$ signal, that is 12×10^{14} spins/g according to the correlation of Table 2. On the other hand, the crystal current and the $g=1.96$ signal appeared to increase inversely about 10% of the expected change. These results suggest that when the oxygen surface coverage is high enough, photoexcitation results in efficient capture of the photoexcited electrons, \ominus , from the conduction band to form O_2^- species according to the reaction scheme:



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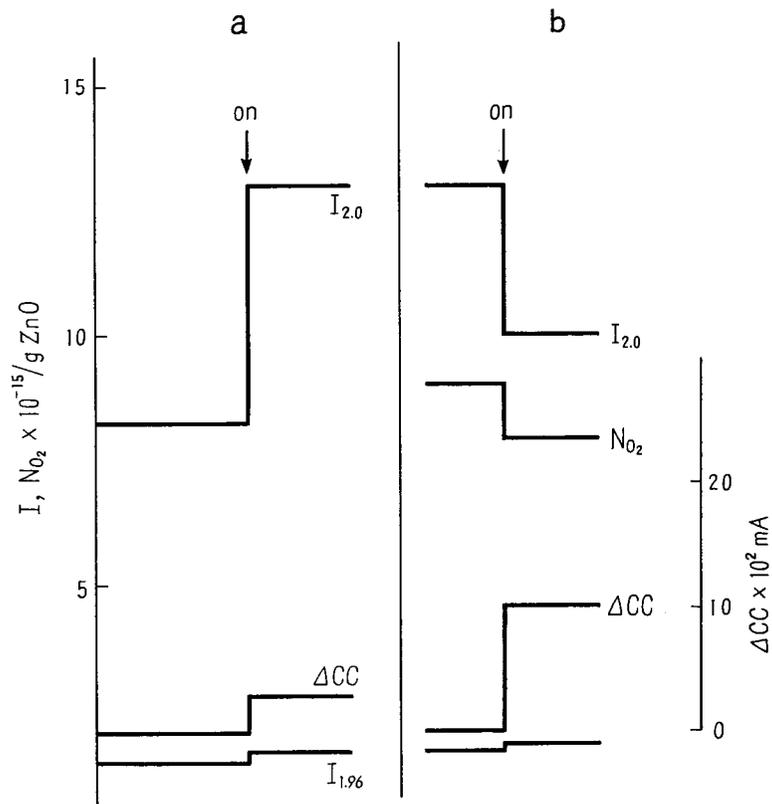


Fig. 3. a: Changes of $I_{1.96}$, $I_{2.0}$ and CC due to photoirradiation under 20 Torr O_2 (ZnO).
 b: Changes of $I_{1.96}$, $I_{2.0}$, CC and N_{O_2} due to photoirradiation under 10^{-4} Torr O_2 (ZnO).



The photoproduced holes, \oplus , are probably trapped at bulk or surface defects.

Photodesorption under Low Oxygen Pressure

The effect of photodesorption could be studied by evacuating the above ZnO to 10^{-5} Torr at room temperature. Upon irradiation the desorption of oxygen, the decrease of the $g=2.0$ triplet signal, and the increase of the $g=1.96$ signal and of the crystal current were observed. The results are shown in Fig. 3 b and Table 3 respectively.

The oxygen desorbed was calculated from the pressure change to be

Takao KWAN *et al.*TABLE 3. Photoeffect for ZnO-O₂ at room temperature.

"reduced": pretreated in vacuo at 500°C.

"oxidized": pretreated in O₂ at 200°C.

| Photoeffect (g ZnO) | Pretreatment of ZnO | | |
|---|------------------------|------------------------|------------------------|
| | "reduced" | "reduced" | "oxidized" |
| Pressure of O ₂ (Torr) | 30 | 10 ⁻⁵ | 10 ⁻⁴ |
| Time of photoirr. (min) | 30 | 20 | 15 |
| N _{O₂} (molecules) | | -11 × 10 ¹⁴ | 7 × 10 ¹⁴ |
| I _{2.0} (spins) | 47 × 10 ¹⁴ | -28 × 10 ¹⁴ | 0 |
| I _{1.96} (spins) | 1.6 × 10 ¹⁴ | 2 × 10 ¹⁴ | 1.5 × 10 ¹⁴ |
| CC (mA) | 3 × 10 ⁻² | 10 × 10 ⁻² | |

11 × 10¹⁴ molecules per g ZnO and appeared to be considerably smaller than the decrease of the g=2.0 signal due to O₂⁻ (-ΔI_{2.0} = 28 × 10¹⁴ spins) as shown in Table 3. The latter decrease is expected to correspond, according to the correlation of Table 2, to an increase of the crystal current of 20 × 10⁻² mA. However, the observed change of the crystal current was only 10 × 10⁻² mA. Such a tendency was also obtained in other experimental series, especially remarkable when the system was well evacuated at room temperature. This unbalance may be explained partly by the formation of neutral oxygen species, which remain adsorbed after the reaction of O₂⁻ species with photoproducted holes:



and also by a simultaneous reaction leading to a transformation of oxygen species such as



The reaction (5) indicates that photoproducted electrons do interact with negatively charged oxygen species during the *photodesorption* of oxygen. Indeed, photoirradiation under a little higher oxygen pressure caused the pressure of oxygen to decrease to some extent.

These results indicate that the amount of neutral oxygen molecules on the surface of ZnO controls the direction of the photoresponse. We shall

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consider the possibility of reaction (5) in the next section.

Photoadsorption on Oxidized ZnO

Photoadsorption of oxygen was found to occur for an oxidized ZnO sample in accordance with the previous finding of FUJITA and KWAN.⁶⁾ A ZnO sample was heated at 200°C for 30 minutes under 20 Torr oxygen and evacuated to 2.5×10^{-4} Torr at room temperature. Irreversible photoadsorption was observed, as indicated by the last column of Table 3, when such a treated ZnO was irradiated at room temperature. The amount of oxygen adsorbed was 7×10^{14} molecules/g but the spin density of the signal around $g=2.0$ did not change appreciably. Since the number of O_2^- species, *i. e.* the $g=2.0$ signal, was almost constant even though oxygen molecules were adsorbed on ZnO, it seems likely that reactions (3) and (5) occurred in a way to maintain the concentration of the O_2^- species constant and also to increase the total surface concentration of charged oxygen species.

In another experimental series, the ZnO prepared just as above was photoirradiated under 20 Torr oxygen for 30 minutes. We found that the $g=2.0$ signal increased and this fact is in accordance with the above speculation; that is reaction (3) now dominates over (5).

3-2 Photoadsorption and Photodesorption of O_2 on TiO_2

Only photoadsorption of oxygen has been reported on TiO_2 .¹⁰⁾ In that study the sample was prepared by drying suspensions of TiO_2 in acetone or water at room temperature. We have found³²⁾ that irradiation of wavelengths of 300 to 410 $m\mu$ caused photodesorption of oxygen to take place on a TiO_2 sample, if the sample was outgassed in vacuo at 500°C, just as the case of ZnO. This result was obtained by measuring simultaneously the change of both ESR signals due to adsorbed oxygen species and of residual oxygen pressure.

Because of the similarity of the data to those obtained on ZnO, we shall not describe the results here. Instead, we shall report some significant photo-behavior of a defect in the bulk of TiO_2 .

To begin with, let us review shortly the ESR spectrum of the TiO_2-O_2 system. When a white TiO_2 sample was outgassed in vacuo less than 10^{-5} Torr at 500°C for one hour, its color was bluish gray, and two ESR signals were observed. One was a narrow singlet signal ($g=2.002$, $\Delta H=4.6$ G) and the other a broad and asymmetric signal (near $g=1.95$, $\Delta H=110$ G) observable only at lower temperatures ($-195^\circ C$). These two signals were tentatively assigned to O^- species and Ti^{3+} respectively.³²⁾ Similar signals have been obtained by KASANSKII,³³⁾ SCHUIT³⁴⁾ and TURKEVICH.³⁵⁾

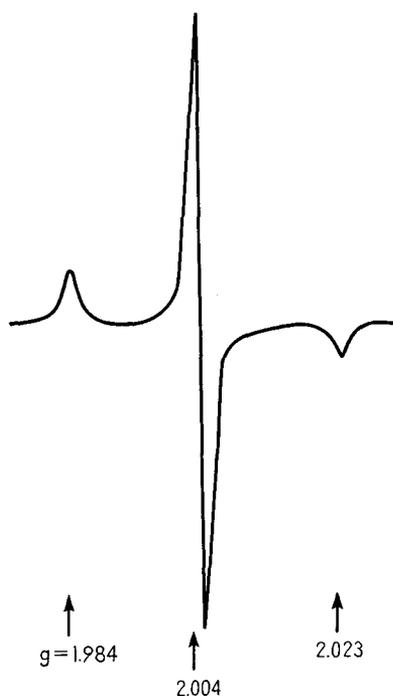


Fig. 4. "Signal-D" originated from the bulk of TiO_2 .

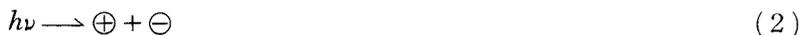
We obtained a triplet ESR spectrum of $g=1.984$, 2.004 and 2.023 , as shown in Fig. 4, when the TiO_2 sample was pretreated in an O_2 atmosphere at 500°C . This signal showed no pressure broadening effect, suggesting that it originated from the bulk of TiO_2 . The intensity of this signal was greatest when the oxygen pressure during the pretreatment was in the range from 0.1 to 10 Torr. The signal disappeared upon outgassing at 500°C in vacuo, but it reappeared upon subsequent exposure to O_2 , SO_2 or NO_2 .

Since the triplet signal reappears by adding such electron acceptor gases, it seems very likely that the signal is characterized by a lattice defect deficient in electron. We shall call this signal as "signal-D" and investigate its photobehavior under low and high oxygen pressures. The "signal-D" may correspond to what TURKEVICH *et al.*³⁵⁾ assigned to " O_2^+ ".

Photoadsorption under High Oxygen Pressure

After outgassing the TiO_2 sample at 500°C for one hour, the sample was pretreated with 8 Torr oxygen at the same temperature for 15 minutes to produce signal-D. The sample was then exposed to 40 Torr oxygen at room temperature and irradiated at wavelengths in the range of $300\text{--}410\text{ m}\mu$.

As shown in Fig. 5, the intensity of signal-D, denoted as I_D , increased upon irradiation, and it decreased gradually upon turning off the light. The phenomena may be explained by assuming the following reactions which involve photoadsorption of oxygen:



where $\boxed{\uparrow}$ indicates signal-D or the unoccupied lattice defect.

The decay of signal-D, when the light was switched off, would probably be explained by reaction (7) in which excess photoproduced electrons in the

Photoadsorption and Photodesorption of Oxygen

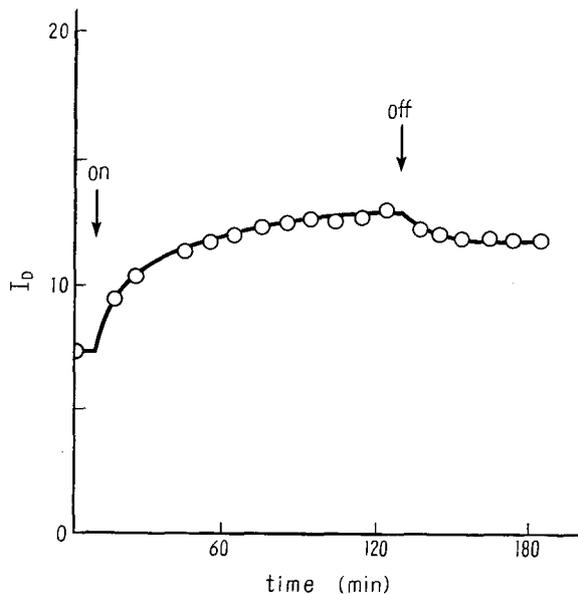


Fig. 5. Changes of I_D due to photoirradiation under 40 Torr O_2 (TiO_2).

conduction band combine with the unoccupied lattice defects :



Photodesorption under Low Oxygen Pressure

When the TiO_2 sample was irradiated under residual oxygen pressure as low as 10^{-4} Torr, an increase of oxygen pressure and a decrease of the $g=2.009$ signal due to adsorbed oxygen species³²⁾ were observed, both of which suggest that photodesorption of oxygen took place. As the $g=2.009$ signal did not overlap with the central line ($g=2.004$) of the signal-D, it was possible to determine the change of the $g=2.009$ signal due to photoirradiation.

On the other hand, the I_D was found to decrease, as shown in Fig. 6, contrary to the high pressure case. Starting ordinate was not the same with that of Fig. 5 since some preliminary measurements were made between runs concerning the effect of wavelengths on I_D as will be described in the next section.

The photodesorption of oxygen obtained under low oxygen pressure may be interpreted by the following reactions :



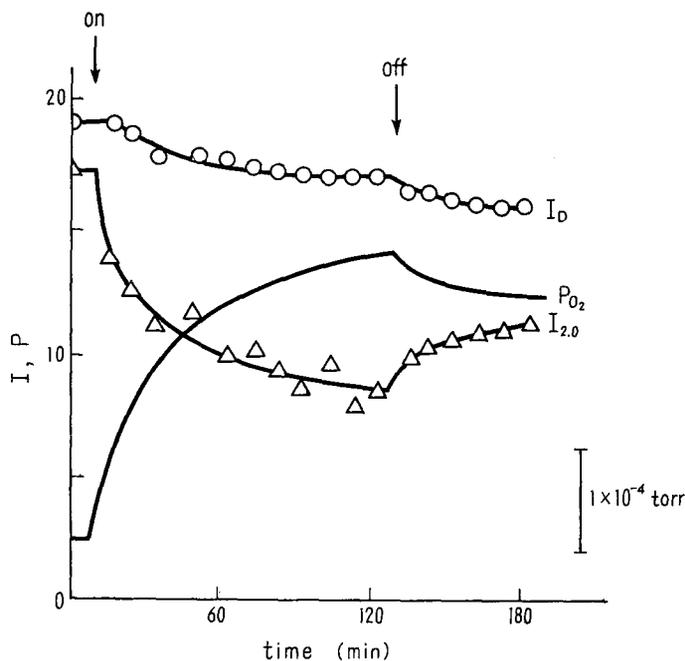
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Fig. 6. Changes of I_D , $I_{2.0}$ and P_{O_2} due to photoirradiation under 10^{-4} Torr O_2 (TiO_2).



Dependence on Wavelengths

So far we employed excitation wavelengths ranging from 300 to 410 $m\mu$, *i. e.* wavelengths near the band gap of TiO_2 (3.0 eV). It was considered that if signal-D was associated with a defect level in the band gap it could be excited at longer wavelengths, and the idea was tested experimentally. The results are shown in Fig. 7. Here, the measurements were carried out under 50 Torr oxygen pressure although the effect of wavelengths was essentially independent on the pressure.

A marked decrease of I_D was observed when wavelengths longer than 500 $m\mu$ were employed whereas irradiation at less than 500 $m\mu$ caused I_D to increase remarkably. The decreasing portion of the curve is probably associated with the excitation of electrons from the valence band to the defect level while the increasing portion is associated with excitation from the defect level

Photoadsorption and Photodesorption of Oxygen

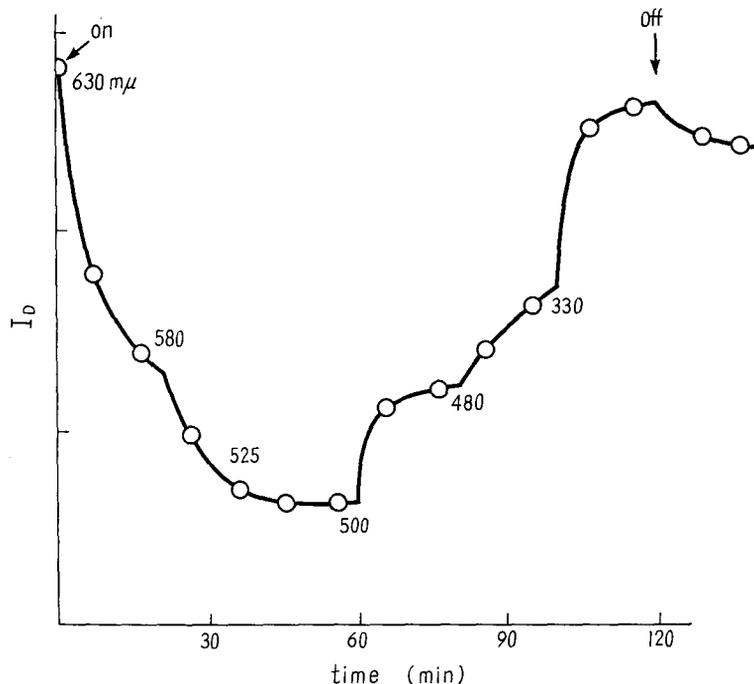


Fig. 7. Effect of wavelengths on I_D (TiO_2). $P_{\text{O}_2} = 50$ Torr.

to the conduction band. If so, the energy level of the signal-D is estimated to be about 2.4 eV from the bottom of the conduction band.

3-3 Photoadsorption of O_2 on ZrO_2

We have found that ZrO_2 , at room temperature, photoadsorbs oxygen under low and high pressures when irradiated in the wavelength range of 250–380 mμ. The ESR spectrum for oxygen adsorbed on ZrO_2 was essentially the same with those for ZnO and TiO_2 ; a triplet signal at $g = 2.003$, 2.008 and 2.027 developed gradually when a small quantity of oxygen was introduced to a ZrO_2 sample at room temperature. The growth of the triplet signal was rather slow in the dark, but developed very fast when the solid was irradiated, suggesting that photoadsorption of oxygen takes place. The process is shown in Fig. 8 for a low oxygen pressure.

It was thought that photodesorption of oxygen would occur on a highly outgassed sample just as the case of ZnO and TiO_2 . However, we were unable to demonstrate this experimentally for a ZrO_2 sample outgassed at 700°C; the sample, presorbed by oxygen at room temperature with residual pressure ranging from 10^{-2} to 10^{-5} Torr, gave rise to only photoadsorption.

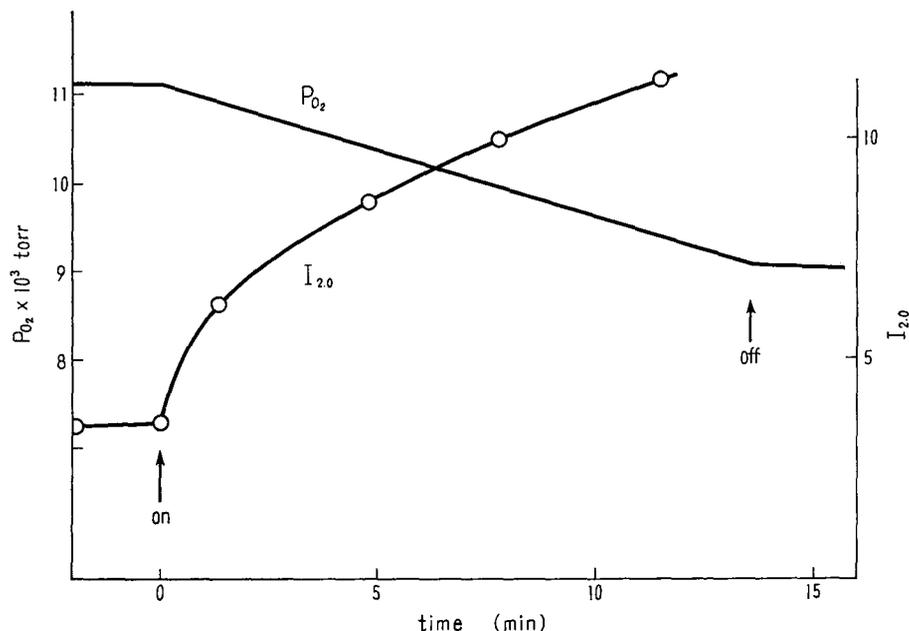
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Fig. 8. Changes of $I_{2.0}$ and P_{O_2} due to photoirradiation (ZrO_2).

The heat of formation of ZrO_2 is 258.1 kcal/mole, and much greater than that of ZnO (83.3) or TiO_2 (218.7). The absence of photodesorption of oxygen on ZrO_2 is probably due to difficulty in reaching a *reduced* state.

Conclusions

1. If a semiconductor sample such as ZnO is in a *reduced* state, photodesorption of oxygen takes place whereas it gives way to photoadsorption for a sample in an *oxidized* state. The result agrees qualitatively with the electron theory of Wolkenstein; for acceptors like oxygen, photoadsorption takes place for a lower Fermi level while it turns out to be photodesorption for a higher Fermi level. The *discovery* of photodesorption of oxygen on TiO_2 and the lack of success to detect photodesorption of oxygen on ZrO_2 may be interpreted from such a viewpoint.

2. If the interaction of oxygen with a semiconductor such as ZnO is reversible, as has been assumed in the theory, photoadsorption observed under high oxygen pressures is a natural consequence of the theory. However, the interaction is only irreversible. If the Fermi level of a semiconductor sample is determined by the pretreatment and independent on residual oxygen pres-

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tures, excess neutral oxygen molecules on the surface play a dominant role for the photoadsorption.

3. In photodesorption of oxygen the predominant interaction is between positive holes and negatively charged oxygen species on the surface ; in photoadsorption the predominant interaction is between adsorbed oxygen species and photoproduced electrons. Electrons and positive holes are involved in both photoadsorption and photodesorption phenomena.

4. Defects in the bulk of semiconductors such as TiO_2 participate in the photoadsorption and photodesorption of oxygen, and indeed the photoresponse is observed to be dependent on the wavelengths of irradiation.

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